CARBON BLACK FEEDSTOCK FROM LOW TEMPERATURE CARBONIZATION TAR

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About three years ago Ashland Oil and Refining Company management initiated a modest coal liquids research program. This program was aimed at accumulating basic technology and at providing a basis for more extensive studies. During the early stages research consisted primarily of literature surveys and scouting experiments. It was concluded from this initial work that low temperature carbonization (LTC) of coal could supply coal liquids at attractive values when considering the current economic conditions.

Discussions with FMC Corporation established their willingness to cooperate in supplying tar from their LTC-pilot plant for experimental work. The FMC unit was constructed under sponsorship of the Office of Coal Research (OCR). This project is designated as Char-Oil-Energy-Development and has the acronym of COED.

The COED process utilizes multiple stage, fludized-bed pyrolysis with increasing stage temperatures to drive off the volatile matter at controlled rates and temperatures so that a high percentage of the coal is converted to gas and condensable oil products. Coal is crushed and dried and fed to the first stage vessel, where it is fluidized in hot recycle gases generated from combustion of some of the product gas or char. The coal then proceeds from the first stage, which is nominally at 600°F, to the subsequent stages where it is subjected to increasing temperatures of 850, 1000 and 1600°F. Heat for the second and third stages comes from burning some of the char with oxygen in the fourth stage. The gases from the fourth stage flow countercurrent to the solids through the third stage to the second stage, from which most of the volatile products are collected. A small percentage of the volatiles comes from the first stage. A small amount of char is recycled to the third and to the second stage to help provide the heat necessary to maintain the vessel temperatures. The volatile products from the pyrolysis are condensed and separated.

The project COED tar that was the feedstock for all work described in this paper was derived from Illinois #6 coal.

Ashland's position as a supplier of refinery products and carbon black--through the United Carbon division--had a significant influence on the selection of the research program goals for processing of LTC tar. The primary objective of this program was to produce carbon black feedstock from all or a portion of the LTC coal liquids. A product of this nature would require a minimum amount of upgrading and would utilize heretofore unmarketable fractions of the coal liquids. Secondly, emphasis was placed on converting the fractions unsuitable for carbon black feedstock into products compatible with normal refinery operations.

Other researchers have tried many techniques to upgrade LTC tar including coking, thermal cracking and hydrogenation. Products ranging from coke to gasoline with some intermediate chemicals are commonly reported in the literature. Probably the point most common to the work of these various groups was the fact that the processes were uneconomical. Processes to produce chemicals from LTC coal liquids failed because these materials could not be obtained by simple processing schemes.

DISCUSSION

An initial quantity of project COED full range coal liquids was obtained from FMC for characterization. A preliminary inspection of the coal liquids showed the following:

Moisture, Volume Percent	4.5-5.0
Benzene Insolubles, Weight Percent	0.5
Quinoline Insolubles, Weight Percent	3.0

This analysis indicated that removal of the particulate matter and moisture would be the minimum treatment for producing carbon black feedstock from the tar.

Initial Processing Scheme

The processing scheme used to produce the three initial samples is shown in Figure 1.

The tar was heated until fluid and blended with benzene in a 1:1 volume ratio in order to reduce the tar viscosity sufficiently to permit centrifugation for solids removal and for a subsequent azeotropic distillation to remove the water. Table 1 presents an analysis of the dry, essentially solids-free tar.

The Bureau of Mines Correlation Index (BMCI) is a measure of the quality of a carbon black feedstock. Feedstocks with a BMCI below 70 are unacceptable; feedstocks with a BMCI of 120 and above are considered ideal. The LTC tar physical properties--low gravity and high 50% boiling point--result in a very high, calculated, Bureau of Mines Correlation Index for this liquid. However, subsequent experimental data indicates the BMCI is apparently valid only for materials that are predominantly hydrocarbon; i.e., do not have high percentages of hetero atoms, such as oxygen, nitrogen and sulfur. As shown in Table 1 the COED LTC tar contains significant quantities of O, N and S. A sample of the dry, solids-free LTC tar--sample A in Figure 1--was taken for evaluation as carbon black feedstock.

The dry, solids-free, full range coal liquids were next vacuum fractionated to produce a -530°F overhead cut and a +530°F (at atmospheric pressure) bottoms fraction. The +530°F bottoms material was evaluated as carbon black feedstock; it is designated as sample B in Figure 1. The -530°F overhead was catalytically hydrotreated in a fixed bed 3/4 inch diameter reactor at moderate temperature and pressure. Analytical data revealed a significant change from feed to product. Marked decreases were noted in boiling range and gravity at high volumetric yield. A major reduction in O, N, and S content was observed. The product contained high concentrations of naphthenes and aromatics; this in conjunction with its boiling range, characterized the product as a potential refinery reformer charge stock.

A third sample for carbon black feedstock evaluation--C in

Figure 1--was prepared by solvent extraction (2:1 solvent to oil ratio) of the +530°F coal liquids. The solvent was a typical reformate (°API=53.4) containing about 61% P+N and 38% A. The extraction yielded an insoluble raffinate (275°F S.P. pitch-like material) and the extract fraction. After stripping off the solvent, the extract yield was about 74 weight percent. Ten gallons of this material were evaluated as carbon black feedstock.

An analysis of carbon black feedstock samples B and C is shown in Table 2. Samples A, B and C were evaluated at United Carbon's pilot plant in a 2 inch furnace. All coal derived samples were handled in an identical manner, and a standard carbon black feedstock was also processed in the pilot unit for comparison. The coal liquids carbon black product was compounded into a standard rubber formulation. This formulation was evaluated against rubber compounded from an ISAF control carbon black and the carbon black produced in the pilot plant from the standard feedstock. The full range and vacuum reduced samples (A and B, respectively) produced an inferior carbon black in low yields. The low structure and low modulus exhibited by the rubber formulations were particularly noticeable. The extracted sample (C) produced a low yield of carbon black, but the quality was nearly equal to the standard feedstock, with the exception of having only a slightly lower structure. Yield data is presented in Table 3.

These results indicate the extraction is more of a de-ashing step than a true extraction and that the high oxygen content of the tar suppresses carbon black yield. Carbon black quality is detrimentally affected by sodium, potassium and other metals normally found in coal ash and in low grade feedstocks. These metals cause carbon black structure (chain length) to be low. The yield from +530°F tar was approximately 75% of the standard feedstock and was encouraging from a research standpoint. Nevertheless, the value of the 75% yield feedstock is much less than 75% of the going rate for high quality feedstocks, due to the combination of higher feedstock consumption per pound of carbon black, higher fuel gas consumption per pound of carbon black and reduced reactor capacity.

Hydrotreating-Microreactor

Because of the high oxygen content (~8%) of the dry, solids-free tar and its detrimental effect on carbon black yield, it was decided to attempt to selectively hydrotreat the tar with the objective of removing the oxygen, nitrogen and sulfur without ring saturation. Fixed bed, catalytic hydrotreatment of the tar was conducted at a moderate temperature and intermediate pressure in a 3/4 inch diameter reactor. The process was studied by evaluation of composited reactor effluent and off-gas samples from consecutive test periods of 19 to 24 hours duration.

A hydrocarbon liquid yield on feed of about 86 weight percent and an aqueous yield of about 3% were obtained. Hetero atom removal based on the feed and composited effluent samples was over 90% for sulfur, over 60% for oxygen, and nearly 40% for nitrogen. Hydrogen consumption for this level of processing was estimated at 1200 to 1500 SCF/bbl. of feed. Material balance data indicated that hetero atom removal accounted for the largest portion of the hydrogen consumed with most of the remaining hydrogen used appearing as cracked products in the off gas.

The hydrotreated composited product was fractionated into a -600°F refinery feedstock and a +600°F carbon black feedstock. The weight percent yields were about 58% overhead and 42% bottoms.

The +600°F bottoms are characterized below. This table shows a considerable upgrading of the feedstock over that previously produced and indicates that a potential carbon black yield comparable to the standard carbon black feedstock should be obtained from the hydrotreated +600°F bottoms.

CARBON BLACK FEEDSTOCK COMPARISON

	Wt. %		Ratio	Carbon Black
	C	H	C/H	Yld. lb/gal.
Standard C.B. Feedstock	90.2	8.2	11.0	3.75
Extract from +530° Fraction	83.7	7.6	11.0	2.74
Hydrotreated +600° Fraction	89.1	8.0	11.1	--

Carbon black yield data on the hydrotreated +600°F tar could not be obtained since the 3/4 inch reactor hydrogenation techniques produced only one gallon of full range hydrotreated tar. Pilot scale carbon black feedstock evaluations require a minimum sample of ten gallons.

The experimental data from the 3/4 inch reactor served as the basis for planning further processing of project COED's LTC tar. It was decided to attempt hydrotreating of the dry, full-range tar in a 4 inch diameter reactor to produce sufficient +600°F material for pilot scale evaluation as carbon black feedstock.

Hydrotreating-Four Inch Reactor

As a result of the above work, an additional 150 gallons of full-range COED liquids was obtained for processing through the 4 inch reactor. The coal liquids "as received" contain sufficient particulate matter and water to cause operability problems on a pilot scale. As discussed earlier, the tar was processed initially by centrifugation and azeotropic distillation to remove solids and moisture. The following table shows the results of this processing:

	Tar As Received	Tar Processed
Ash	0.83	0.44
Quinoline, Insolubles	3.6	1.8
Benzene, Insolubles	4.3	7.3

Characterization of the dry, solids-free tar showed it to have essentially the same analysis as shown in Table 1.

After processing to remove water and solids, the full-range LTC tar was hydrotreated in the 4 inch reactor system for hetero atom removal at approximately the same conditions which were used in the 3/4 inch reactor.

Processing in the 4 inch unit represented a feed rate scale up of about 160 over that of the 3/4 inch reactor. Severe temperature control problems resulted from the scaled-up operation due to the exothermic nature of the reactions taking place. The desired isothermal reactor profile for optimum selectivity and hetero atom removal could not be maintained. Fluctuations between low temperatures (increased naphthene formation) and high temperatures (catalyst deactivation and corresponding reduction in deoxygenation) resulted in more oxygen and hydrogen and less carbon in the reactor effluent than the project goals. Carbon content of the hydrotreated composite was 86.5 weight percent, somewhat below the 87.7 weight percent obtained in the 3/4 inch reactor processing. Figure 2 illustrates the general effects of temperature on product composition.

Overall, considerable difficulty was experienced in obtaining smooth operation of the 4 inch reactor; however, the entire amount of feed available was processed. The liquid hydrocarbon yield was about 89 weight percent on feed, and the aqueous yield was about 3 weight percent. This compares very well with the results from the 3/4 inch reactor.

The table below compares hetero atom removal based on overall feed and composited product data for the 4 inch reactor and 3/4 inch reactor:

HETERO ATOM REMOVAL-WEIGHT PERCENT

	Oxygen	Nitrogen	Sulfur
4 inch Reactor	58	16	83
3/4 inch Reactor	62	38	93

Hydrogen consumption was estimated at 2000 SCF/bbl. based on an overall material balance and hetero atom removal. Hydrogen consumption is thus higher than the 1500 SCF/bbl. obtained in small scale processing. This may be attributed to increased naphthene formation and increased hydrocracking in the 4 inch reactor.

The hydrotreated tar was fractionated to produce a -600°F overhead cut and a +600°F bottoms fraction. The yields on dry, solids-free tar were about 46 volume percent overhead and 54 volume percent bottoms. The -600°F fraction will be discussed later in this paper.

The +600°F Fraction

The +600°F fraction (Table 4) was shipped to the United Carbon laboratories for pilot scale carbon black production. The carbon black produced was then evaluated as described earlier by compounding in a standard rubber formulation. The results of these tests can be summarized as follows:

1. The material handled satisfactorily in the pilot scale reactors.

2. The carbon black produced from the hydrotreated +600°F coal liquids has only a slightly lower modulus with comparable tensile, elongation and abrasion resistance and approximately 10% lower structure as compared to a carbon black which was made from a standard carbon black feedstock.

3. Yield of carbon black from the hydrotreated +600°F tar is only about 80% of the standard feedstock, 3.10 lbs/gal. vs. 3.97 lb/gal., at essentially the same surface area.

4. A 60% reduction in oxygen did not significantly change the carbon black yield. Apparently sufficient naphthene formation had occurred in the 4 inch reactor to counteract the reduction in oxygen. Carbon to hydrogen ration and oxygen content are summarized below:

	% Oxygen	C/H
Standard Feedstock	0	11.0
+530°F Extracted Tar	8	11.0
+600°F Hydrotreated Tar	3	10.2
Raw Tar	9	10.9

In summary, the initial attempt to produce a carbon black feedstock from LTC tar via selective hydrogenation followed by fractionation resulted in an acceptable quality black and demonstrated the technical feasibility for this processing route. Yield was not as high as desired and may be attributed to not achieving process goals for hetero atom removal during hydrotreatment.

Further Processing of +600°F Fraction

The original process goal was to achieve a +600°F bottoms material with a 90 weight percent carbon content, since this level is comparable to the standard carbon black feedstock. The following table shows the ultimate analysis of the untreated +600°F tar, the hydrotreated +600°F tar and the standard carbon black feedstock:

Ultimate Analysis, Wt. %	Standard Carbon Black Feedstock	Raw Tar +600°F	Hydrotreated Tar, +600°F
Carbon	90.20	82.6	86.97
Hydrogen	8.20	7.55	8.50
Oxygen	-	8.88	2.97
Nitrogen	-	0.96	0.92
Sulfur	1.60	1.30	0.30

In an effort to achieve 90 weight percent carbon content material, the hydrotreated +600°F tar from the 4 inch reactor was catalytically hydrotreated again at a moderate temperature and pressure in a 2 inch diameter reactor. The second pass hydrotreated +600°F tar is characterized in Table 5. The yield of the material is approximately 35 volume percent of the dry, solids-free COED tar. Note that the project goal of 90 weight percent carbon content was very nearly achieved.

A sample of this second pass hydrotreated +600°F tar was forwarded to the United Carbon division and was processed through their pilot plant to produce carbon black. Performance of this tar in the pilot scale carbon black reactor was practically identical to that of the standard carbon black feedstock.

Data from rubber samples compounded with carbon black from the second pass hydrotreated +600°F tar show the black to be nearly equal to the carbon black produced from the standard feedstock at identical reactor conditions. Some of the pertinent data from these tests are given in Table 6. A carbon black yield of about 90 weight percent of the standard was obtained.

The -600°F Fraction

A laboratory inspection of the -600°F fraction from the 4 inch reactor is shown in Table 7. Although the aromatics content of this particular material was not determined, a -600°F cut from the 3/4 inch reactor study, with very similar properties, contained well over 70 volume percent aromatics by FIA analysis. This indicates the -600°F fraction would be a highly desirable refinery feedstock. However, the hetero atom concentration of this cut is too high to permit processing by conventional refinery techniques. For this reason, second pass hydrotreating of the -600°F cut was studied.

Pilot studies indicated a reactor configuration with a fairly high residence time would be required to effectively remove the hetero atoms in the second pass catalytic hydrotreating step. Such a reactor was constructed and successfully operated with the -600°F fraction (Table 7) feed to produce 5.5 weight percent water and a second pass -600°F liquid hydrocarbon product in 92.2 weight percent yield with the following properties:

-600°F SECOND PASS
HYDROTREATING EFFLUENT

°API	29.5
FIA, LV%	
P + N	33.2
O	1.0
A	65.0
Hetero atoms, ppm	
S	35
N	620
Bromine No.	2.2

Hetero atom concentrations have been reduced sufficiently by this operation to permit processing of the material in conventional refinery units.

The -600°F second pass hydrotreating effluent was fractionated into five fractions: (1) IBP-160°F, 0.9 LV%; (2) 160-360°F, 42.5 LV%; (3) 360-410°F, 12.1 LV%; (4) 410-550°F, 32.5 LV%; (5) 550-600°F, 12.0 LV%, for laboratory and pilot scale evaluation as refinery feedstock. The IBP-160°F cut was not processed further since in practice this would probably be included in the reformer charge because of its small quantity and its composition. The 160-360°F fraction was characterized as reformer chargestock on the basis of its naphthene content and boiling range. Results of the pilot scale reforming are shown in Table 8. Note specifically the very high blending value of the reformate, its high aromatic (90+%) content and the high gas make which is estimated to be 92% hydrogen in a recycle operation.

Laboratory evaluation of the 360-410°F and 410-550°F fractions indicated they should be combined and subjected to a relatively severe hydrotreating step, then fractionated to a 410°F cut point. The -410°F portion with a 98.5 F-1 clear octane would then be blended into gasoline, and the highly aromatic (12.0 °API) 410-525°F bottoms would be an excellent hydrodealkylation feedstock since it has a naphthene potential of over 57 weight percent on feed.

The 550-600°F fraction could be marketed as #2 fuel oil.

ECONOMICS

The preliminary economics of a commercial scale LTC tar processing facility have been estimated based on a pilot plant and laboratory data. The economics assume a 10,000 ton/day coal carbonization unit is located adjacent to the tar processing facility. This unit, while not directly included in the economics, supplies a low cost source of 11,906 bbl/day of full-range LTC tar. Figure 3 is a block flow diagram of the proposed processing scheme starting with the full-range LTC tar.

A capital investment of $13,100,000 has been estimated for the processing units shown in Figure 3, with the exception of the carbon black facility, which is not included in the economics. A discounted cash flow of 20% can be realized on this investment with full-range LTC tar valued at $1.62/bbl. and the following values placed on the various products:

Carbon Black Feedstock	-	7¢/gallon
#2 Fuel Oil	-	9¢/gallon
Gasoline Blending Stock	-	14¢/gallon (102+ Octane No.)
Benzene	-	23¢/gallon
Naphthalene	-	4.5¢/lb.
H_2 Consumed or Generated	-	30¢/1000 SCF

SUMMARY

The technical feasibility of hydrotreating full-range LTC tar to produce a highly aromatic residue boiling above 600°F, with low hetero atom content, has been demonstrated. The hydrotreated +600°F fraction has been processed on a pilot scale to an acceptable quality carbon black in good yield.

The lower boiling material (-600°F fraction from hydrotreating full-range LTC tar) when nearly free of hetero atoms is a highly aromatic material ideally suited for processing in conventional refinery equipment to yield valuable products.

Preliminary economics, based on pilot plant data, indicate the overall LTC tar processing scheme can realize a good DCF rate of return on investment, when reasonable product values are assumed.

ACKNOWLEDGMENT

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FIGURE 1

INITIAL PROCESSING SCHEME

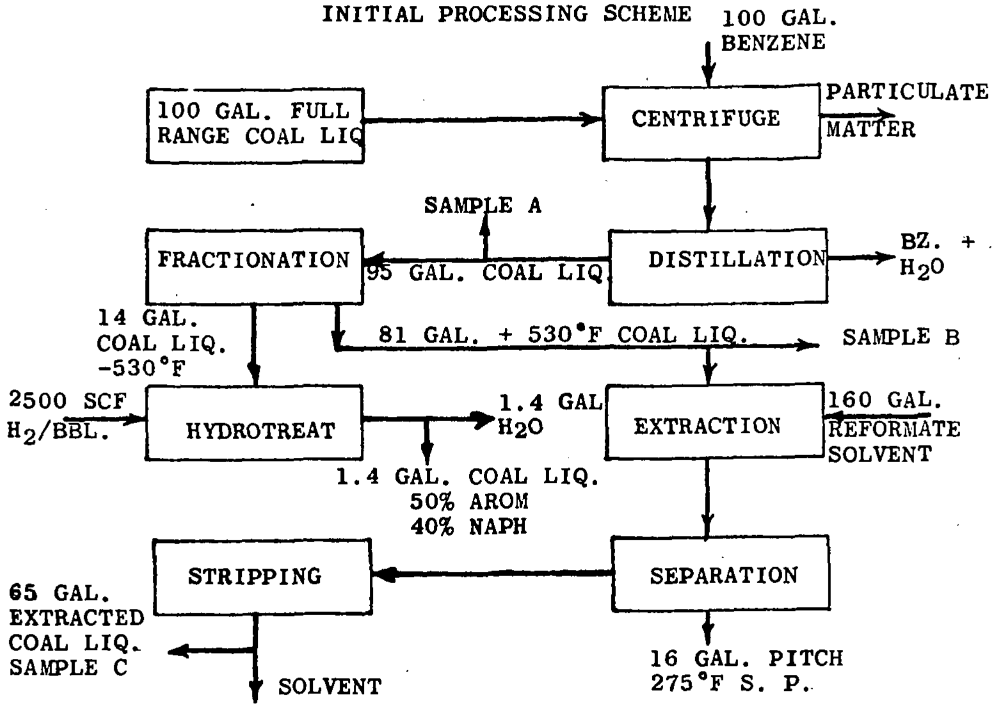

TABLE 1

PROJECT COED FULL RANGE COAL LIQUIDS
(DRY, SOLIDS-FREE)

SAMPLE	A
DISTILLATION, °F	
5%	457
10%	486
30%	701
50%	831
70%	932
80%	Cracking
QUINOLINE INSOLUBLE, WT. %	0.33
°API AT 60°F	-6.1
ASH, WT. %	0.13
CONRADSON CARBON, WT. %	18.4
CORRELATION INDEX	140
ULTIMATE ANALYSIS, %	
CARBON	82.42
HYDROGEN	7.55
OXYGEN	8.74
NITROGEN	1.10
SULFUR	0.9

TABLE 2

PROCESSED PROJECT COED COAL LIQUIDS

SAMPLE	B	C EXTRACTED
DISTILLATION, °F	+530°F CUT	+530°F CUT
IBP	–	450
5%	525	521
10%	581	571
20%	680	672
30%	742	741
40%	794	Cracking
50%	836	
60%	Cracking	
BENZENE INSOLUBLE, WT. %	12.0	0.013
°API AT 60°F	-8.7	-7.2
ASH, WT. %	0.18	0.022
CONRADSON CARBON, %	21.7	14.96
CORRELATION INDEX	157	150
ULTIMATE ANALYSIS, %		
CARBON	82.71	82.61
HYDROGEN	7.89	7.55
OXYGEN	8.90	8.88
NITROGEN	1.16	0.96
SULFUR	1.00	1.30
POTASSIUM, PPM		4.7
SODIUM, PPM		8.0

TABLE 3

CARBON BLACK YIELD DATA

FEED	YIELD (POUNDS/GALLON)
STANDARD C. B. FEEDSTOCK	3.75
FULL RANGE COAL LIQUIDS -- A	2.70
+530°F FRACTION OF FULL RANGE COAL LIQUIDS -- B	2.64
EXTRACT FROM +530°F FRACTION -- C	2.74

FIGURE 2. EFFECT OF TEMPERATURE ON PRODUCT COMPOSITION

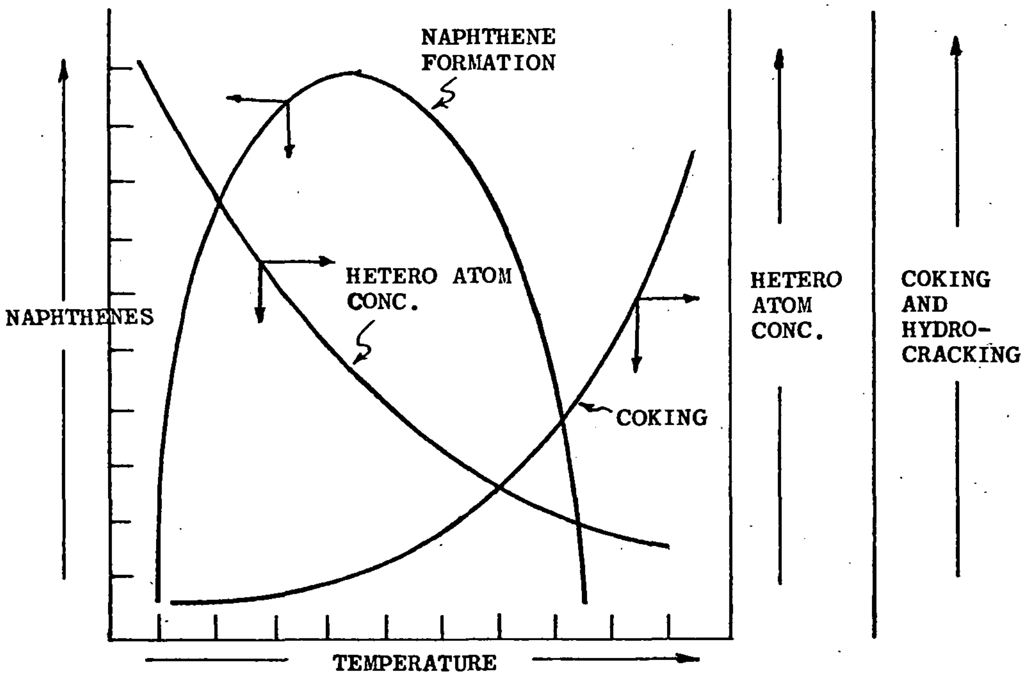

TABLE 4

+600°F HYDROTREATED FRACTION OF PROJECT COED COAL LIQUIDS

DISTILLATION, °F	
10%	655
30%	708
50%	781
70%	866
90%	Cracking
GRAVITY, °API AT 60°F	0.4
RAMSBOTTOM CARBON, WT. %	3.8
CORRELATION INDEX	121.9
ULTIMATE ANALYSIS, WT. %	
CARBON	86.97
HYDROGEN	8.50
OXYGEN	2.97
NITROGEN	0.92
SULFUR	0.30
ASH	0.07

TABLE 5

LABORATORY INSPECTION OF SECOND
PASS HYDROTREATED +600°F FRACTION

DISTILLATION, °F	+600°F BOTTOMS
5%	615
10%	629
30%	668
50%	714
70%	767
90%	866
95%	912
GRAVITY, °API AT 60°F	4.2
BENZENE INSOLUBLE, WT. %	0.094
QUINOLINE INSOLUBLE, WT. %	0.018
RAMSBOTTOM CARBON, WT. %	2.74
CORRELATION INDEX	111.7
ULTIMATE ANALYSIS, WT. %	
CARBON	89.38
HYDROGEN	8.48
OXYGEN	1.54
NITROGEN	0.60
SULFUR	0.04
ASH	0.02

TABLE 6

LABORATORY EVALUATION OF RUBBER SAMPLES

SAMPLE		ISAF CONT.C	COAL LIQUIDS	STANDARD	COAL LIQUIDS	STANDARD	COAL LIQUIDS
CURED AT 293°F	MIN.						
MODULUS AT 300% (PSI)	120	2100	2280	2380	2330	2320	2300
COLLECTED YIELD #/GAL.			3.83	4.23	3.82	3.97	3.51
TENSILE STRENGTH (PSI)	120	4300	3740	4130	4270	3770	4300
% ELONGATION AT BREAK	120	510	420	435	450	420	445
SURFACE AREA, (M^2/GM)			126	112	112	139	137
ANGLE ABRASION GMS LOSS/HR.	90	10.4	12.4	12.5	10.3	10.6	10.1
% SWELL EXTD.STK		92.1	105.6	102.0	109.3	105.6	109.3
DBP ABRASION		114.8	138.6	138.5	140.1	139.8	141.4

TABLE 7

-600°F FRACTION OF HYDROTREATED
PROJECT COED COAL LIQUIDS

ASTM DISTILLATION, °F	
IBP	280
10%	370
30%	416
50%	452
70%	492
90%	546
95%	Cracking
GRAVITY, °API AT 60°F	17.6
BROMINE NUMBER	65.7
ULTIMATE ANALYSIS, WT. %	
CARBON	83.48
HYDROGEN	10.27
OXYGEN	5.38
NITROGEN	0.88
SULFUR	0.13
ASH	0.002

TABLE 8

REFORMATE FROM 160-360°F FRACTION OF SECOND
PASS HYDROTREATED -600°F COAL LIQUIDS

LIQUID YIELD ON FEED	90.1 VOL. %
GAS MAKE, SCF/BBL. FEED	1025
GRAVITY, °API	33.5
ASTM DISTILLATION, °F	
IBP	168
5%	208
10%	220
30%	244
50%	266
70%	288
95%	232
E.P.	368
OCTANE NUMBERS	
F-1 CLEAR	101.4
F-1 + 3 G. TML.	105.9
BLENDING OCTANE NUMBER	114.7

FIGURE 3

CARBON BLACK FEEDSTOCK
FROM
LOW TEMPERATURE CARBONIZATION TAR
ESTIMATED MATERIAL BALANCE